EFFECT OF DIFFERENT TACKIFIERS ON PROPERTIES OF STYRENE-GRAFTED NATURAL RUBBER (SNR) AND DEPROTEINIZED NATURAL RUBBER (DPNR) LATEX FILMS

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LIST OF ABBREVIATIONS

APS	Ammonium persulfate
BA	Butyl acrylate
C	Carbon
CI	Coumarone-indene
DPNR	Deproteinized natural rubber
DRC	Dry rubber content
DTG	Derivative thermal gravimetric analysis
ENR	Epoxidised natural rubber
FTIR	Fourier transform infrared spectroscopy
GR	Gum rosin
HIPS	High-impact polystyrene
IPDT	Integral procedure decomposition temperature
IPN	Inter-penetrating network
MEK	Methyl ethyl ketone
MMA	Methyl methacrylate
MST	Mechanical stability time
MTS	Modified tapioca starch
MW	Molecular weight
NR	Natural rubber
O	Oxygen

PBA	Poly(butyl acrylate)
PR	Petro resin
PS	Polystyrene
PSA	Pressure-sensitive adhesive
Si	Silicon
SNR	Styrene-natural rubber
TGA	Thermogravimetry analysis
TMTD	Tetramethyl thiuram disulphide
TPE	Thermoplastic elastomer
TSC	Total solid content
UTS	Unmodified tapioca starch
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

%	percentage
%T	transmittance percentage
^{o}C	degree celcius
A	absorbance
cm	centimeter
cm^{-1}	per centimeter
cP	centiPoise
g	gram
kg	kilogram
mg	miligram
mL	mililiter
mol/g	mol per gram
mol/kg	mol per kilogram
mm/min	milimeter per minute
MPa	megaPascal
N/m	Newton per meter
N/m^2	Newton per meter square
s	second
T_5	temperature at 5% weight loss
T_{max}	peak temperature at maximum decomposition rate
w/w%	weight by weight percent

KAJIAN TENTANG KESAN PELBAGAI JENIS PEMELEKAT KE ATAS SIFAT-SIFAT FILEM LATEKS GETAH ASLI STIRENA (SNR) DAN GETAH ASLI TERNYAHPROTEIN (DPNR)

ABSTRAK

Getah asli stirena (SNR) dan getah asli ternyahprotein (DPNR) telah dirumuskan dengan pemelekat *coumarone-indene* (CI), gam rosin (GR) dan petro resin (PR) kepada perekat larutan menggunakan pelarut toluene. Kanji terubahsuai butil akrilat (MTS) dan kanji tak terubahsuai (UTS) digunakan sebagai pemelekat dalam perekat lateks dan sebagai pengisi bagi komposit SNR dan DPNR. Semua perekat diuji dari segi kekuatan gelung, kekuatan kupasan dan kekuatan ricih dan komposit diuji dari segi kekuatan tegangan, kestabilan terma dan morfologi patah. Ujian perekatan menunjukkan bahawa kemelekatan gelung dan kekuatan kupasan meningkat sehingga tahap pemelekat optima tetapi merendahkan kekuatan rich dengan peningkatan kandungan pemelekat. Pemelekat CI mencapai kekuatan kupasan yang tertinggi dalam perekat SNR/CI pada 166 N/m dan DPNR/CI pada 124 N/m. Sebagai perekat, kanji MTS meningkatkan kekuatan ricih untuk perekat lateks SNR dan DPNR masing-masing sebanyak empat kali ganda dan 65% pada kandungan 40 bahagian per seratus getah (bsg). Peningkatan kekuatan ricih ini dikaitkan dengan peningkatan kekuatan kohesif dalam matriks SNR dan DPNR. Penambahan kanji MTS dan UTS menyebabkan peningkatan kestabilan terma untuk komposit SNR dan DPNR. Komposit SNR/MTS dan DPNR/MTS mencapai kekuatan tegangan yang lebih tinggi daripada komposit UTS, membuktikan bahawa MTS adalah pengisi penguat manakala UTS adalah pengisi lengai. Kesan penguatan MTS disokong oleh morfologi patah untuk komposit SNR/MTS yang menunjukkan bahawa saiz zarah MTS adalah lebih kecil daripada zarah UTS.

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ABSTRACT

Styrene-grafted natural rubber (SNR) and deproteinized natural rubber (DPNR) rubber were formulated with coumarone-indene (CI), gum rosin (GR) and petro resin (PR) tackifiers into solution adhesives with toluene as a solvent. Butyl acrylate-grafted starch (MTS) and unmodified starch (UTS) was used as tackifiers in latex adhesives and as fillers in SNR and DPNR composites. The adhesives were subjected to loop tack, peel strength and shear strength tests, and the composites were tested in terms of tensile strength, thermal stability and fracture morphology. The adhesion tests showed that the loop tack and peel strength of the solution adhesives increased up to an optimum loading but decreased their shear strengths with increased tackifier loading. The CI tackifier conferred the highest peel strength in SNR/CI adhesive at 166 N/m and DPNR/CI adhesive at 124 N/m. As a tackifier, MTS starch increased the shear strength of SNR and DPNR latex adhesives by four-fold and 65% respectively at 40 parts her hundred rubber (phr) loading. The shear strength improvements was attributed to the improvement of cohesive strength in the SNR and DPNR matrices. MTS and UTS starch incorporation increased the thermal stability of SNR and DPNR composites. SNR/MTS and DPNR/MTS composites exhibited higher tensile strength than UTS composites, which proved that MTS is a reinforcing filler and UTS acts as inert filler. The reinforcement effect of MTS was supported by the fracture morphologies of the SNR/MTS composites, which showed that the MTS particles were significantly smaller than UTS particles.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Natural rubber is an essential raw material for many fields of applications such as medical, industrial, automobile, and household items. It is used in the manufacturing of various products such as rubber gloves, textile linings, tire components and adhesives. The natural rubber latex is commonly tapped from the *Hevea brasiliensis* rubber tree as a white, milky sap that is essentially a colloid of rubber particles suspended in a protein serum (Kalia & Avérous, 2011). The pure chemical makeup of purified natural rubber is poly(isoprene), which can be artificially produced via chemical means and is the base for all synthetic rubbers. The long repeating chains of poly(isoprene) in natural rubber give rise to rubber's unique properties such as its elasticity, high green strength and the ability to strain-crystallize upon stretching (Riegel & Kent, 2007).

The synthetic rubber market has grown significantly over time as the demand for synthetic rubber has risen sharply, particularly after natural rubber shortage crisis during the second World War period. The International Rubber Study Group (IRSG) has placed the world rubber production in 2011 to be around 26.0 million tonnes, which is shared between 10.9 million tonnes of natural rubber and synthetic rubber for the remaining 15.1 million tonnes (www.lgm.gov.my, 2011). Synthetic rubber has overtaken natural rubber in terms of the global production and consumption, as it covers a wide range of rubbers, including poly(isoprene), styrene-butadiene rubber, poly(butadiene), acrylonitrile-butadiene rubber and poly(urethane) rubber (Groover,

2010). In most cases, the products made from synthetic rubber are almost identical in properties to natural rubber counterparts. The most significant advantage of synthetic rubber is the absence of proteins commonly found in the natural rubber serum that causes rubber allergies in humans. However, these allergy cases are still a minority in the human population and mostly involved unpleasantness or skin irritation in the affected individuals. The advantages of using natural rubber still far outweigh the allergy problems associated with it (Rom & Markowitz, 2006). Despite the significant developments of synthetic rubber, natural rubber remained of the best rubber material in the industry, mostly due to its cost benefits and superior tack properties compared to its synthetic counterparts.

Although natural rubber has high green strength and elasticity, it is rarely used without modification. This is due to the fact that rubber has many limitations in its natural state, such as its susceptibility to ozone cracking and poor solvent resistance (Dick & Annicelli, 2001). In fact rubber modification is an extensively researched field, where new compounds are constantly developed to further improve the properties and usefulness of the rubber compounds. The most direct process through rubber modification is by addition of additives into the rubber compound to improve certain properties of the rubber compound or to add new attributes to the existing rubber matrix (Angellier et al., 2005c). The most commonly used rubber additive is fillers, which can be employed for reinforcing or non-reinforcing purposes. The black colour of automobile tyres is to the addition of carbon black fillers into the rubber component of the tyre, making it more durable and resistant to heat during its service life. In fact, carbon black is used in a lot of rubber products such as engine mounts and dampers because it imparts higher mechanical properties and abrasion resistance to the rubber compound (White, 1995). Apart from fillers, other additives

that are added into natural rubber production include plasticizers, coupling agents, dispersion agents, anti-oxidants and curing agents.

Another route for rubber modification is to modify the chemical structure of the rubber molecules to improve certain attributes or to increase the resistance of the rubber to various hostile elements. The chemical structure of the repeating unit of rubber contains an unsaturated double bond, which holds endless potential for chemical modification. A commonly used vulcanization strategy is via sulfur crosslinking, which involves inserting sulfur chain bridges in between the long rubber molecular chains. The resultant properties of the sulfur-vulcanized rubber varies depending on the length and distribution of the sulfur chain bridges, which can be tailored to suit the desired properties of the end rubber product. For example, shorter sulfur chains impart higher rigidity to the end rubber, where else longer sulfur chains improve the aging properties of rubber compound (Kotz et al., 2011). In fact, the unsaturated bonds provide active sites for grafting with other monomers to create new rubber compounds. Extensive research has been done for rubber-grafted polymers using styrene (Chattopadhyay & Sivaram, 2001; Chuayjuljit et al., 2005; Nampitch & Buakaew, 2006), acrylic (George et al., 2003; Moreno-Chulim et al., 2003), and vinyl monomers (Lenka et al., 1985; Kangwansupamonkon et al., 2005).

Deproteinized natural rubber (DPNR) latex has almost the same composition of natural rubber latex with the exception of thin protein layers that envelops the NR dispersion particles. The main application of DPNR in the current market is to alleviate the rubber protein allergy issue in certain individuals due to the sensitization to the protein layers. Another benefit of DPNR latex is the improvement of the grafting efficiency of other graft polymers into the DPNR molecular chains because the protein layers present in NR latex interferes with the graft polymers and

negatively affects the grafting efficiency of the graft polymer unto the NR rubber chain (Fukushima et al., 1997). DPNR latex was used in this work as the base rubber latex for the synthesis of styrene-grafted natural rubber (SNR) latex as it has significantly lower protein content and to ensure the maximum grafting efficiency of styrene unto DPNR latex. It was also used as a comparison latex to SNR in terms of adhesive and composite properties.

Styrene-grafted natural rubber (SNR) has been developed for the last decade, mostly for the improvement of impact modifiers in rubber-reinforced thermoplastic compounds. In the case of high-impact polystyrene (HIPS), the SNR rubber component is used as an interface material between the polystyrene matrix and the reinforcing butadiene component to promote better impact force distribution. This is because the impact properties of the HIPS is limited to the interface between the matrix and the particulate reinforcement, and SNR is designed as a interfacial promoter between the two distinct materials that are usually incompatible with each other and thus improve its impact performance (Neoh & Hashim, 2004). Novel applications are being researched for this SNR rubber, as this is the central rubber matrix used in this work.

Natural rubber has been used in adhesives for more than a century. Adhesives are used in virtually all industries ranging from food to production as an essential material to bond to 2 or more other substrates together. Natural rubber latex has been found to be tacky when it dried, a property that enabled early rubber adhesives to bond porous materials such paper, wood, and even other rubbers together. This is because rubber has excellent peel strength, fatigue and impact properties but lacks in shear strength and high heat performance (Ebnesajjad, 2010). Due to the low strength and thermoplasticity of the rubber adhesives, it is not generally used in structural

applications. However, its long tack retention properties makes it ideal for pressure-sensitive applications since the coated surface will bond for extended lengths of time after application of the adhesive. Examples of products that fall into this category is self-adhering envelopes, post-it notes and transparent tapes (Benedek, 2004).

Natural rubber adhesives are usually heavily modified with other synthetic chemicals and resins such as tackifier, plasticizers, fillers and anti-oxidants to further improve their adhesion abilities or other attributes such as viscosity and shelf-life. There are naturally-occuring tackifiers as well as synthetic tackifiers. Examples of natural tackifiers are rosin acid derivates and their esters. Synthetic tackifiers are based on either aromatic or aliphatic petrolueum-based resins. Tackifiers normally have low molecular weights and are in resinous forms, but have glass transition temperatures and softening temperatures that are significantly above room temperature (Kotz et al., 2011). Its main purpose is to impart tack and desirable viscoelastic properties in the formulation of the adhesive. In fact, the tackifier is the main ingredient that is used to tailor and refine the adhesion and processing performance in the adhesive formulation. Generally, tackifiers are used to raise the glass transition temperature of the rubber adhesives that normally has a glass transition temperature below that of room temperature. Other requirements of a good tackifier is that it must possess low surface tension to readily wet the substrate and that is must be compatible with the base rubber in the adhesive system (Brockmann et al., 2008).

1.2 Problem statement

While natural rubber (NR) has been extensively used a base for manufacturing adhesives, it has limited usefulness as it has inherently low strength and thermoplasticity. The natural rubber adhesives are rarely used for demanding applications, especially in structural applications where high strength is a predominant requisite. Natural rubber adhesives also have a limited suitable operating temperature range from 65^{o}C to 95^{o}C, and cannot withstand continuous loads during its service life (Drake, 1997). Thus, styrene-grafted natural rubber (SNR) is evaluated as an alternative to natural rubber to overcome the limitations of natural rubber.

Natural rubber adhesives are usually supplied in a solvent solution to facilitate good flow and coating properties. The conventional choice of solvents is usually industrial, non-green solvents such as toluene, benzene and acetone. The solvents are an essential part for certain adhesive systems such as contact adhesive, white glue and rubber cements, as the maximum adhesion properties is achieved from the removal of the solvents in the adhesive system. However, the use of solvents poses an environmental risk and health hazard for living organisms. For instance, most solvents are highly volatile and flammable, in addition to being highly toxic (Wypych, 2001). Thus, there is a pressing need to minimize or eliminate the use of solvents in adhesives systems, and more focus is being emphasized in water-based adhesives.

Most natural rubber formulations incorporate some form of tackifying agents to further improve its adhesive performance. The formulation for natural rubber adhesives, especially in tackifiers, has been researched exhaustively (Fujita et al., 1998; Leong et al., 2003; Poh & Chang, 2006; Poh & Kwo, 2007). However, there is

almost no data on the effects of tackifiers on the styrene-natural rubber adhesive formulations. This work is done to further improve the knowledge of tackifier effects on the attributes and performance of SNR based rubber adhesives. However, the addition of tackifiers onto the adhesive system may alter the characteristics of the adhesive system in other critical aspects of the adhesive system, especially if large loadings of tackifier are needed to achieve the optimum adhesion properties. Thus, it would be necessary to evaluate changes in the properties of the SNR rubber adhesive systems with regard to the addition of the tackifier system.

Since natural rubber has been extensively used as an adhesive matrix, this work will focus on styrene-grafted natural rubber (SNR) is studied as an alternative matrix for producing pressure-sensitive adhesive formulations. The performance of the SNR matrix was compared to its natural rubber counterpart in terms of adhesion performance and compatibility with the tackifier systems. Since the tackifier parameters predominates the adhesion properties of the adhesive, this work investigated the effects of adding various tackifiers on the properties of styrene-grafted natural rubber latex. The optimum loading of the tackifier for each adhesive formulation to achieve maximum adhesion properties was investigated.

1.3 Research objectives

1. To investigate the effect of CI, GR and PR tackifier loading on the loop tack, peel strength and shear strength of SNR and DPNR solution adhesives
2. To investigate the effect of the modified tapioca starch on the loop tack, peel strength and shear strength of the SNR and DPNR latex adhesives
3. To investigate the effect of modified tapioca starch on the tensile and thermal decomposition properties of SNR and DPNR composites

1.4 Research scope

In this work, styrene-natural rubber (SNR) was synthesized from deproteinized natural rubber (DPNR) latex via in situ polymerization process and used a base rubber in preparing adhesive and composite formulations. The tapioca starch was gelatinized and grafted with butyl acrylate (BA) monomer to produce modified tapioca starch (MTS). The particle size of the MTS, unmodified tapioca starch (UTS), and SNR was investigated, as well as the effect of starch loading on the viscosity of the starch/SNR compounds. MTS was used as tackifier in SNR and DPNR latex adhesives and investigated as reinforcing filler in SNR composites. Coumarone-indene, gum rosin and petro resin was dissolved in toluene and used as tackifiers in SNR and DPNR solution adhesives, and their adhesion properties such as loop pack, peel strength and shear strength were investigated. The thermal stability of the SNR/starch and DPNR/starch formulations was studied using thermogravimetry analysis (TGA). The fracture surface of the SNR/MTS composites was studied using scanning electron microscopy (SEM) to investigate the effects of starch loading on the failure deformations of the SNR/MTS composites.

1.5 Outline of thesis structure

Chapter 1 gave a brief introduction on natural rubber, the various modification routes to improve it functionality, the development of natural rubber in the adhesive field and the use of tackifiers with adhesives. The research objectives and research scope of this work was outlined.

Chapter 2 explored the details of related publications to this work, including natural rubber properties, previous research into SNR, the mechanism of styrene grafting unto DPNR, adhesive materials and their classifications, theories of adhesion, natural rubber adhesives, tackifiers, the use of starch as additives, various starch modifications and starch-based adhesives.

Chapter 3 detailed the materials used in this work and the experimental procedures carried out to synthesize the samples as well as the characterization methods that was used to study the effects of various tackifiers on the properties of SNR.

Chapter 4 reported the results obtained from this work and the discussion on the obtained results including the particle size analysis of the starch and rubber particles, the viscosities of the various SNR adhesive, the adhesion properties of the SNR/tackifier and SNR/starch adhesives, the thermal behaviour of the SNR compounds and the tensile properties of the SNR/starch composites.

Chapter 5 summarized the findings of this work and concluded with some suggestions for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural rubber latex

Natural rubber (NR) is one of Malaysia's most renowned commodities due to the increasing global demand for natural rubber latex and its rubber product derivatives. The demand for natural rubber has been spurred on by booming rubber and latex industries in Malaysia and around the world. Other than the established application of NR in barrier applications such as gloves, balloons and adhesives, NR lattices are pioneering new advances in the biomedical field, such as a drug delivery system in guided bone regeneration (Herculano et al., 2009) and in vascular prosthesis (Neves-Junior et al., 2006).

The source of natural rubber is the latex tapped from rubber trees from the species *hevea brasiliensis*. In the modern polymer field, the term 'latex' denotes a stable colloidal dispersion of a polymeric substance in an aqueous medium. Natural rubber latex, being the most widely known plant latex, is a stable colloidal dispersion of cis-1,4-polyisoprene, as of high molecular mass in an aqueous medium. It comprises of two phases, a dispersion medium and a disperse phase. The dispersion medium is also referred to as the 'serum' of the latex, and is denoted as the aqueous fluid which exudes from the latex when colloidal destabilization and phase separation has occurred. The other phase, known as the disperse phase or discontinuous phase, is a composition of spherical particles of the high molecular weight polymer with particle sizes ranging from 100 nm to 1000 nm. The rough composition of fresh natural rubber latex is given in Table 2.1 (Bateman, 1963).

Table 2.1: Composition of raw natural rubber latex (Bateman, 1963)

Constituent	Amount (%)
Rubber	30.0 – 40.0
Protein	1.0 – 2.0
Lipids	0.9 – 1.2
Carbohydrates	1.0 – 1.2
Inorganic matter	0.5 – 0.6
Water	55.0 – 60.0

The stability of the NR latex is maintained by the slightly negative charges on the rubber particles that discourage agglomeration of the particles. However, inherently present bacteria in the latex serum will produce organic acid that will neutralize this negative charge and cause destabilization of the latex. Thus, freshly tapped NR latex is immediately preserved with ammonia and sometimes together with secondary preservatives, such as tetramethyl thiuram disulphide (TMTD), to neutralize any bacterial acids to preserve the consistency of the latex for further processing (Kurian & Peter, 2007). At this point the NR latex becomes known as 'preserved NR latex'.

Due to the low rubber content in preserved NR latex, it is never utilized commercially in the rubber industry. Instead, the NR latex must be concentrated to increase the rubber content of the latex to about 60.0 – 61.0% to standardize the NR latex, increase its economic viability and to comply with the requirements of latex product manufacturers. There are four main practices to concentrate the preserved NR latex, namely evaporation, creaming, centrifugation and electrodecantation. Out of these methods, centrifugation is the most widely used method to concentrate the preserved NR latex due to its high speed and high consistency. Although there are numerous designs for latex centrifuge machines, the basic concept used is the same.

It consists of a rotating bowl in which a set of conical metallic separator discs is enclosed (Bhowmick & Stephens, 2001).

For centrifuged NR latex, there are two usual preservative systems depending on the amount of ammonia used to preserve the colloidal stability of the NR latex. Thus, the preserved latex with the higher ammonia content is denoted as High Ammonia (HA) latex, while lower ammonia content is used in Low Ammonia (LA) latex. The quality parameters of the concentrated NR latex are strictly assessed under ISO 2004:1997 given in Table 2.2.

Table 2.2: Specification for centrifuged NR latex concentrate under ISO 2004

Parameter	**HA latex**	**LA latex**	**ISO test method number**
Total solids content, min; %	61.5	61.5	124
Dry Rubber content, min; %	60.0	60.0	126
Nonrubber solids, max; %	2.0	2.0	-
Alkalinity, as ammonia, on latex weight;%	0.6(min)	0.29(max)	125
Mechanical stability time, min; s	650.0	650.0	35
Coagulum content, max; %	0.05	0.05	706
Volatile fatty acid number, max	0.20	0.20	506
Potassium hydroxide number, max	1.0	1.0	127
Copper content, max; mg/kg solids	8.0	8.0	1654
Manganese content, max; mg/kg	8.0	8.0	1655
Sludge content, max; %	0.1	0.1	2005

Along with styrene-butadiene rubber (SBR), natural rubber latex is classified as commodity latex, in the sense that NR latex is used in very large quantities, have very narrow applications, and have large global overcapacity, low prices and low profit margins. However, NR latex concentrate has found critical applications in the

manufacture of dipped products such as gloves, gloves, teats, soothers, and latex thread in which the material need to have a rubbery consistency, high elasticity and non-porous behaviour. The second largest application for NR latex is in the adhesive industry such as pressure-sensitive adhesives and hot-melt adhesives used in various common products such as envelopes and seals (Beswick & Dunn, 2004).

2.2 Deproteinized natural rubber latex (DPNR)

Although NR latex has many uses, the protein allergy issue still remains a great drawback to expand the market of NR latex globally. This is due to the protein layers such as hevamine, hevein and rubber elongation factor, which are found in the natural rubber latex dispersion phase. Some studies have found that the corn starch powder, an additive to ease glove donning and removal, can act as carriers for the allergens from the NR latex (Acello, 2002). Hence, synthetic rubber latex remained the choice latex to alleviate the consumer concerns that the allergy issue may arise in latex products used in critical applications such as medical or food industries.

Since then, research has been geared in order to remove the inherent layer of protein present in NR latex. Ichikawa et al. (1993) has proposed that the protein can be leeched out of the latex by addition of an enzyme to hydrolyze the protein layer and then followed by centrifugation. However, removing the protein layer surrounding the latex particles would cause the NR latex to become unstable because the latex particles lose their slightly negative charges that acts as a stabilizing wall between the particles. Thus, sodium dodecyl sulfate was used as a surfactant to stabilize the NR latex during the deproteinization process. Latex treated in this manner would have much lower extractable protein content of approximately 0.02

w/w%, compared to 0.40 w/w% protein content in untreated NR latex concentrate. This class of latex is known as deproteinized natural rubber (DPNR) latex.

Removing the protein layer surrounding the latex particles has another benefit other than the alleviation of the protein allergy issue. Previous research done by Fukushima et al. (1997) has shown that the protein layers produces side reactions with grafting agents, thus reducing the grafting efficiency of other polymers into the NR latex. The removal of this protein layer has thus removed one of the main barriers of grafting of monomers into the latex, as the monomers can now readily penetrate into the latex particles without the protein layer obstruction. Another method to deproteinize natural rubber latex by Pukkate et al. (2007) was called urea-deproteinization. This method has a distinct advantage of a lower output time, requiring only 1 hour of incubation time compared to the 24 hours needed for enzymatic deproteinization.

Tho et al. (2002) carried out a comparative study of in situ polymerization of styrene in both DPNR and high ammonia NR lattices. With the same polymerization conditions, the styrene-DPNR system achieved a high styrene conversion of 97 percent without the addition of surfactants. The styrene-high ammonia NR system required the use of surfactant to complete the polymerization of similar reaction time, and yielded a much lower 66 percent styrene conversion, which can be ascribed due to presence of the protein/lipid layer in the high ammonia NR latex.

2.3 Styrene-grafted natural rubber (SNR) latex

Graft polymerization of the styrene onto natural rubber in its latex state gaining widespread recognition in preparing functional organic materials. The resultant styrene-grafted natural rubber (SNR) latex can be classified as an inter-

penetrating network (IPN) latex. Latex IPN's are a unique blend of polymer blends comprising the synthesized of swelling crosslinked seed particles of a polymer with another monomer and polymerizing that monomer in situ. The polymer and monomers are generally incompatible with each other, resulting in phase separation in typical blending routes. However, the IPN lattices showed substantially less phase separation, as the presence of the double networks give rise to finely divided phase domains of both the polymer and the monomer phases (Sperling et al., 1972). This statement has been supported by Kawahara et al. (2003), whom has discovered that a nano-matrix structure may be formed by graft copolymerization followed by coagulation of the resulting latex in which the nano-matrix structure consists of a dispersion of major natural rubber particles in a matrix of minor functional polystyrene particles.

Polystyrene-natural rubber IPNs have been extensively research by Mathew et al. (2001). They studied the effects of initiating systems, crosslink density and blend ratio on the mechanical properties and morphology of the PS/NR IPNs. The initiator dicumyl peroxide was found to impart superior mechanical properties to all the IPNs, compared to benzyl peroxide and azo-bis-isobutyronitrile initiators. Scanning electron microscopy of the IPNs revealed that interfacial improvement of PS and NR phases increased with increasing PS content and PS crosslink density until a certain loading of PS, which in turn caused reduced interfacial interactions due to agglomeration of the PS phase. The increased interfacial improvements was found to improve the IPN's tensile, tear and hardness properties but with reduced elongation at break values. Transmission electron microscopy on the IPNs revealed the nanostructure of PS/NR phase due to the intimate mixing of PS-NR phases with microlevel phase separations.

A study by Arayapranee and Rempel (2008a) revealed that SNR molecules comprised of multiple spheres of soft, inner polymer of natural rubber molecules coated with hard layered shells of styrene molecules. This is significant because the microscopic sphere ensures a monodispersed and uniform particle size of SNR latex that allows for excellent blending characteristics with other fillers, additives and/or curing agents. Increasing the SNR content in prevulcanized NR and SNR blend compounds reduced the tensile and tear strengths but increased the Young modulus and hardness of the compounds. Incorporation of SNR also improved the compounds' resistance to heat, weathering and ozone, making SNR blends suitable for rubber products requiring high modulus and good aging resistance.

Che Man et al. (2008) studied the curing behaviour and mechanical properties of styrene/methyl methacrylate grafted DPNR with varying monomer concentrations of 10 percent, 20 percent and 30 percent. According to the Fourier Transform Infrared (FTIR) analysis, the compound with 10 percent monomer concentration showed no appreciable grafting phenomena, whereas the 20 percent and 30 percent compounds yielded some degree of grafting onto the natural rubber. The cure and scorch times of the grafted rubber compound was increased with increasing monomer content, while the maximum-minimum torque decreased slightly. In terms of mechanical properties, increasing the monomer content created a stiffer rubber compound with reduced elongation at break due to the restriction of chain mobility between the molecular chains by the grafted plastic phase of the monomers.

2.3.1 Mechanism of styrene grafting onto natural rubber

Pukkate et al. (2008) has conducted extensive research on the mechanism of styrene grafting onto DPNR latex. To investigate the grafting mechanism, they found that the molecular weight of the grafted styrene polymer in the grafted copolymer (i.e. DPNR) are dependent upon the number of active sites and the feed of the styrene monomer. Thus, they applied ozonolysis to SNR, followed by size exclusion chromatography on the resultant product to determine its molecular weight.

The obtained results showed that the molecular weight of the grafted polystyrene decreased with increasing initiator amounts. This can be explained that at low initiator concentration, the number of active sites on the rubber particle was too small to reach with all the styrene monomers. As the initiator amount is increased, there is an abundance of active sites for the grafting of polystyrene, causing the average molecular weight of the grafted styrene to decrease.

In the case of monomer concentration, Pukkate et al. (2008) found that the molecular weight of the grafted styrene is low at lower concentrations of monomer feed, and that the molecular weight increased as the monomer feed was increased. The relation between monomer feed and molecular weight is given in Equation 2.1

$$\text{Number of active sites} = [M] \times \text{Conversion} / M_n \qquad (2.1)$$

where [M] is the monomer concentration added initially into the system and M_n is the molecular weight of the grafted polystyrene.

The overall summary of the monomer concentration dependency on grafting efficiency is given in Figure 2.1. At low monomer concentrations, a low monomer conversion and low grafting efficiency was reported. This phenomenon is attributed

to the deactivation of number of active sites due to the deficiency of the monomer feed. However, as the monomer concentration is increased up to 1.5 mol/kg of rubber, the number of active sites increased dramatically, due to the increased availability of monomers to be grafted to the rubber chains. However, at higher monomer concentrations, the number of active sites begin to decrease, owing to chain transfer reactions as shown in Figure 2.2. By increasing the amount of active sites, there is an increasingly higher probability for the active site radicals to be transferred either to another monomer, another polymer chain or another polymer radical group, resulting in decreased conversion of polystyrene, and hence the grafting efficiency of the styrene monomer is decreased if the styrene monomer concentration is too high. (Pukkate et al., 2008).

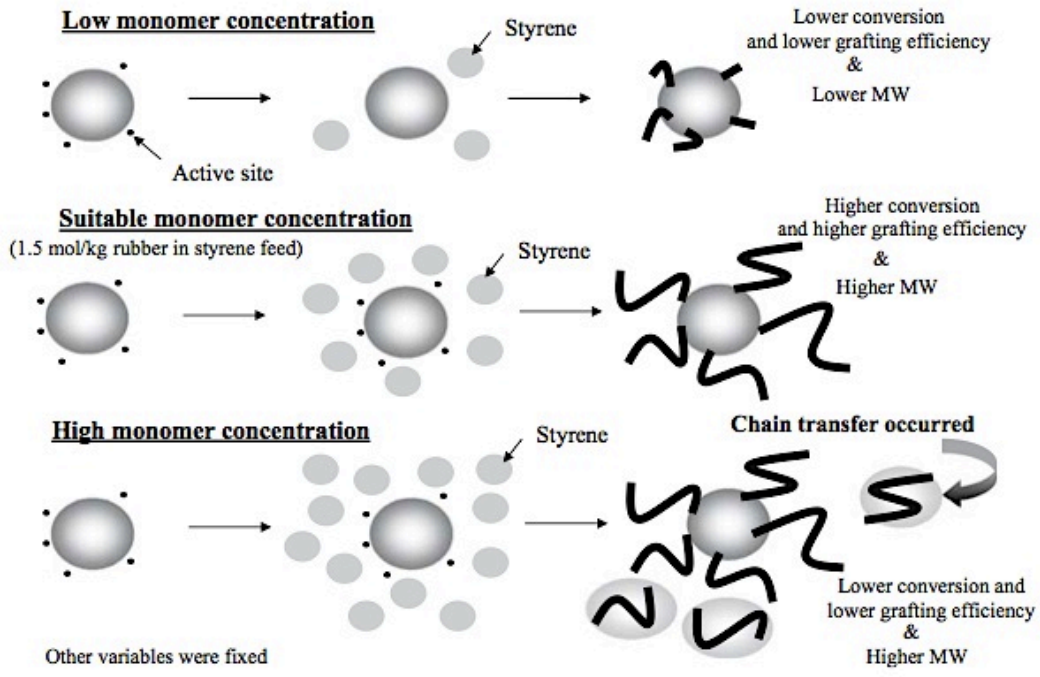

Figure 2.1: Mechanism of styrene grafting onto DPNR particles at various monomer concentrations (Pukkate et al., 2008)

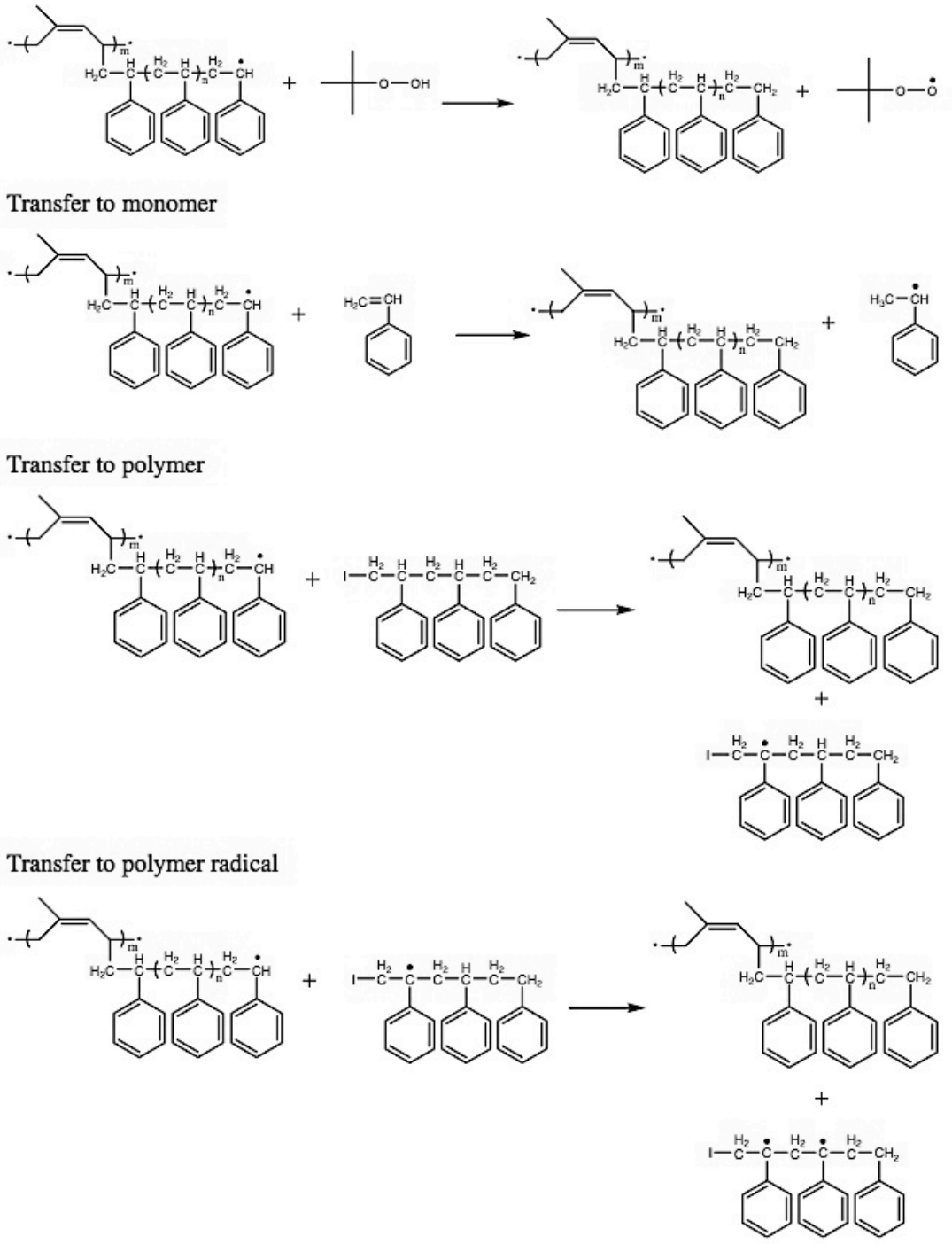

Figure 2.2: Chain transfer reaction in the graft copolymerization of styrene onto DPNR particles (Pukkate et al., 2008)

2.3.2 Emerging applications for SNR

With the development of optimum in situ grafting process for production of SNR latex, novel applications are being discovered for this modified latex. There are four main applications of SNR that are of great interest in regard to industrial applications:

1) high-impact polystyrene
2) thermoplastic elastomers
3) thermoplastic ionomers
4) pressure-sensitive adhesives

I. High-impact polystyrene (HIPS)

High-impact polystyrene (HIPS) composites are composed of a polystyrene matrix enveloping a rubbery natural rubber phase. Both phases are not molecularly compatible and thus the strengthening aspect of the HIPS composite is limited by the interfacial strength between the polystyrene and rubber phases. The addition of a compatibilizer is the most efficient method to increase the interfacial linkages between the two separate phases within the composite. SNR as a compatibilizing agent in HIPS composite was found to improve the tensile strength, impact strength and thermal stability of the composite. This is due to the presence of a highly grafted polystyrene portion in the SNR which is more compatible to the plastic phase than normal NR reinforcement (Neoh & Hashim, 2004). In addition to HIPS, SNR has been found to improve the tensile and stiffness properties of polypropylene-NR blends (Hashim & Ong, 2002), which highlight the usefulness of SNR as a plastic-rubber compatibilizer. Further work by (Neoh et al., 2011) on the effects of vulcanization techniques on the properties of SNR-based HIPS showed that in situ

vulcanization process of SNR gave better tensile strength and impact strength compared to other vulcanization systems. The vulcanization method produced a SNR-HIPS composite with 72 percent higher impact strength compared to commercial HIPS.

II. Thermoplastic elastomers (TPE)

Thermoplastic elastomers (TPE) are a compound material which incorporates the deformation-reversion phenomena of elastomers with the stiffness and processability of thermoplastics. The soft segment of the rubber phase and the stiff segment of the plastic phase are bonded with physical entanglements between the rubber molecular chains and the plastic molecules, as well as the dipole and hydrogen bonds between the molecules. However, the rubber-plastic interface can be further strengthened by introducing chemical linkages between the rubber and plastic phases via graft-copolymerization of styrene onto the rubber. Suksawad et al. (2011) has shown that by careful control of the grafting and processing parameters of styrene onto natural rubber, the resultant TPE composite exhibited an outstanding improvement of mechanical performance. The increase in mechanical properties of the TPE was attributed to the high degree of styrene conversion and high styrene grafting efficiency onto the rubber molecules.

III. Thermoplastic ionomers

Ionomers are polymers that comprise of a major section of hydrophobic backbone molecule with minor section of acid ionic groups. The acid groups are neutralized with metal ions. The formation of phase-seperated ionic aggregates via metallic linkages in the hydrophobic polymer matrix is found to improve mechanical

properties of the polymer matrix. In addition, these linkages are labile at processing temperatures, resulting in ionomers with similar processability as conventional thermoplastics. Work by Xavier et al. (2003) has shown that zinc-neutralized sulfonated styrene-grafted natural rubber could be reproduced consistently and the modified SNR composite showed a ten-fold improvement in tensile properties over the base SNR compound. The thermoplastic elastomer property of the modified SNR was also validated by the retention of the stress-strain properties even after three repeated cycles of mixing and moulding.

IV. Pressure-sensitive adhesives (PSA)

Pressure-sensitive adhesives are conventionally formulated using a tacky elastomer compound in a solvent base. Work done by Neoh et al. (2010) showed that SNR latex has potential as a pressure-sensitive adhesive by testing the adhesion properties of the SNR latex adhesive embedded with curing agents against various substrates. However, the adhesive formulations in that work does not reflect the true potential of SNR as an elastomer base for adhesive formulations as it was just a preliminary study. Thus, further research is needed in order to improve the adhesion properties of the SNR formulations, such as the addition of a suitable tackifier agent to increase it adhesive performance.

2.4 Adhesives

Adhesives are materials that are capable of fastening materials together in desired configurations by surface attachment. The primary attributes of adhesives are the ability to form strong adhesive bonds with a wide range of substrate materials and to retain acceptable bond strength within their specified service lifetime. Although most adhesives do not have excellent bulk properties and therefore necessitate a thin layer of adhesive film for optimum strength, some materials such as epoxies have excellent bulk properties that qualify them as engineering materials and thus can be used in multifunctional applications other than adhesives (Mark, 2007).

The advantages of adhesives are their strong ability to bond to similar and dissimilar materials of different thickness and composition, as well as enabling the joining of complex shape objects that are not usually feasible by other fastening means. Other useful features of adhesives include the smoothening of external joint surfaces, permitting of economic and rapid assembly, as well as uniform distribution of stresses over joined surfaces, weight reduction in critical structures via elimination of fasteners, vibration dampening, minimization of galvanic corrosion, and thermal and electrical insulation (Ebnesajjad, 2008).

However, adhesives have limiting factors, depending on the class. Such limitations may include necessity of surface preparation, long curing times, service-temperature limitations, loss of properties during service, toxicity of flammability during assembly or use, and the tendency of the adhesives to creep under sustained loading (Flick, 1989).

2.4.1 Classifications of adhesives

There are countless amounts of adhesives in the market today due to the maturity of the adhesive industry. Thus, there is no universally acceptable method to classify all the types of the adhesives currently available. However, adhesives can be grouped by various attributes, including their source, function, chemical composition, physical form, and application.

Adhesives can be procured from natural sources, such as starch, casein and shellac, and have the advantages of being low-cost, easy application, and long shelf life. They produce good initial tack but lacks adhesive strength, limiting their usage to porous substrates such as paper, wood and foil. Synthetic adhesives apply to all other adhesives other than natural adhesives.

The majority of adhesives consumed in the world are synthetic due to the specific requirements of the adhesives in performance, applicability and service life. The main groups of synthetic adhesives are thermosetting adhesives, thermoplastic adhesives and elastomeric adhesives. Some modern adhesive hybrids combine two or more chemical groups from thermosetting, thermoplastic or elastomeric groups (Sonnenschein et al., 2008).

Thermosetting adhesives covers adhesives such as epoxy, cyanoacrylates and polyester, and usually supplied in two parts to be mixed before application. The formation of dense crosslinks in thermoset adhesives ensures good resistant to heat and solvents, and shows little deformation under load at elevated temperatures. Most structural applications employ thermosetting adhesives (Petrie, 2006).

Cellulose nitrate, polyvinyl acetate and polyamides are examples of thermoplastic adhesives. These adhesives can be heated without much loss in properties, and are usually single-component systems that harden upon cooling or by